OPTIMIZATION OF REACTOR CONFIGURATION IN COAL LIQUEFACTION

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Introduction

The Department of Energy is sponsoring several Advanced Liquefaction Programs which taken together have the potential to reduce product costs from direct liquefaction to a level of $25 per barrel. HRI has been selected to study the optimization of reactor configurations with a goal of developing a feasible cost-effective processing scheme that will result in an increased overall yield of higher quality distillates. HRI will evaluate combined ebullated-bed and fixed-bed processing, three ebullated-bed stages and interstage feed concentration following the primary reactor. Since the high pressure temperature reactors and associated equipment can comprise 15 to 20% of the capital costs of a grass roots plant, significant savings can result from improved reactor configurations and a decrease in required reactor volume. Further cost reductions will result from expected improvements in product selectivity (gaseous vs liquid) lower hydrogen consumption and better product quality by reduction of heteroatom content and increases in hydrogen content.

The configurations to be studied are :

- Incorporation of a fixed-bed, plug flow reactor after partial conversion and micronization of coal in an upstream CSTR (Continuous Stirred Tank) reactor.

- Comparison of three CSTR reactors with a two-stage system.

- Reconcentration of unreacted solids and residues between stages for improved kinetics in two stage CSTR systems.

An assessment of the preferred temperatures and volumes for multiple stages will also be conducted.

Background

The HRI CTSL[1] Process uses a relatively low temperature first-stage (750-775°F) and a higher second-stage temperature (815-825°F)[1]. The first stage, with more favorable hydrogenation conditions, regenerates the hydrogen-donor capacity of the recycle solvent, while accomplishing a *significant* degree of coal liquefaction (conversion) and production of distillable liquids. The second stage completes the conversion of the coal and produces additional distillable liquids. This process offers a large improvement over earlier processes. With Illinois No. 6 coal over 95% liquefaction of MAF coal has been attained, with a yield of distillate oils ($C_4$750°F) of 78 W% of MAF coal. The CTSL Process employs an ebullated bed of catalyst, which maintains an expanded condition for catalyst and permits passage of large solid particles and avoids problems in dealing with highly viscous liquefied material especially in the first stages of the coal liquefaction reactions.

A principal debit of the ebullated bed reflects the fact that it is a relatively well mixed system with the reactive phase composition (and reaction potential) throughout the reactor corresponding to the product stream composition, in effect a CSTR (Continuous Stirred Tank Reactor) configuration. Such a mode has a kinetic disadvantage relative to that of a plug flow (fixed bed or packed bed) mode where the reaction potential declines progressively throughout the reactor only reaching that of product stream composition at the outlet of the reactor. This disadvantage of ebullated bed reactors is mitigated to a degree by staging, but even the two stage system requires greater reactor volumes especially when targeting very high conversion levels, in excess of 90%.

The first order (for coal concentration) modelling, using CSTR (Continuous Stirred Tank Reactor) reaction equations, has evolved from analysis of coal conversion results from CTSL and various modes of coal liquefaction experience at the HRI R&D center. Application of such a model requires identification of several species of coal types of different reactivity, more or less corresponding to various maceral types identified by petrographic analyses, although the correlating proportions have been developed from the actual two-stage CTSL, or single stage H-Coal, liquefaction results. Classification into three species (one unreactive) has proven adequate to rationalize CTSL experimental results giving coal conversion between 30% and 97% of MAF coal.

Hydrogen-transfer reactions from donor-solvent constituents in the liquid phase are a factor in coal conversion; however, in the correlation of CTSL results where the donor-solvent is generated in situ including this parameter has not been necessary, even though donor quality changes with catalyst deactivation. The overriding factor is that only small changes in conversion have occurred as the catalyst age in CTSL Bench Experiments.

These CTSL correlations are being tested in the current program and will be modified to fit the integrated reaction performance prior to projecting performance of the new reactor configurations.

Using first order kinetic modelling the various reactor configurations can be compared relative to two-stage CSTR performance. *Figure 1* compares reactor volumes to achieve certain coal conversions with Illinois #6 coal. For example as shown, a system following first-order kinetics at 95% conversion would require 130% greater reactor volume as a two-stage than as a plug-flow fixed bed system, all other kinetic factors being equal.

Fixed Bed Reactor

The application of fixed-bed reactors for direct coal conversions was extensively tested in the Synthoil[2] process as a first stage. Problems occurred with plugging, coking and rapid catalytic deactivation. HRI is testing fixed-bed hydrocracking in a second or third stage application where the unconverted coal and ash concentration averages from 10-20% and the particle size is generally less than 325 mesh (44 microns) compared to a typical feed concentration of 35 to 50% and a size of 50 mesh (300 microns). HRI's application as a finishing reactor at low temperature using trilobe catalyst for low pressure drop along with the lower concentration and smaller size should reduce plugging problems and will provide data for modelling.

A simple first-order model with identical rate constants and at a conversions of 95% in two-stages indicates that the CSTR Fixed-Bed would require only 55% of the reactor volume as the CSTR-CSTR configuration.

In modelling the CSTR-Fixed Bed and CSTR-CSTR systems on Black Thunder sub-bituminous, the plug flow option with an isothermal second stage could raise coal conversion by about 3.4% and lower the bottoms plus gas yield by 3.9% of dry coal, with 0.3 W% low hydrogen consumption. The indicated yield of distillates would be 4% higher than in the conventional arrangement, and this yield per unit of hydrogen consumption would be 9% higher.

Three Stage CSTR Systems

The addition of a third ebullated bed in series to the CTSL configuration would assuredly result in closer approach to plug flow-fixed bed potential and involves virtually no processing uncertainties.

The ebullated bed configuration in series differs from previous three stage concepts in control of stage temperatures to obtain an optimum interrelation of hydrogenation and cracking functions. A large part of previous efforts included a high temperature-short contact time pre-reaction of the coal slurry to maximize the degree of coal conversion. Apparently, such a pattern did not promote hydrogenation functions to the degree that would assure the best selectivity to light liquid products, which can be obtained from coupled multistage catalytic system.

It is recognized that three stage testing does not represent a radical innovation, since from the inception of the ebullated bed development it was recognized that the "stirred-tank" effect of the ebullated system has a kinetic disadvantage which could be mitigated in part by staged systems, two, three or more reactors.

However, the effort involves the three ebullated bed configuration largely as a reference for other essential innovations of this program, the use of a fixed bed as the third stage, or the incorporation of a practical method of reconcentration of heavy reactants before entering further staging.

A simple first order kinetic model, with equal temperatures in the stages, indicates that a three-stage system would require 25% less total reactor volume than the two-stage system at a conversion level of 95%.

The three-stage concept can be improved further through interstage product separation and reactant concentration and/or incorporation of a fixed-bed upgrading stage.

Product Stream Concentration

The concentration of primary reactants declines progressively in a plug-flow system and is lower stage-by-stage in a close-coupled, multistage CSTR system. More effective use of reaction space for the conversion of liquid and solid phase reactants can be promoted if their concentrations in the liquid phase could be maintained at higher levels and the hydrogen partial pressure increased. For example, in a three-stage CSTR system with simple first-order kinetics, attaining 95% conversion, the primary reactant concentration being fed to the third stage is about 15% of that in the feed to the first stage. Nominally, if the third stage feed concentration were raised to that of the original feed the proportion of reaction in the third stage could be correspondingly increased. Calculations based on the simple first-order model indicate that a three-stage system of CSTR reactors with reconcentration of the second stage product going to the third stage to obtain the same content of the reacting components as in the first stage feed would require only 43% as much total reactor volume to attain 95% conversion as would be needed in a conventional two-stage system with no interstage feed concentrations. Use of an interstage vapor/liquid separator offers the opportunity to increase the reactant (650°F$^+$ slurry) concentration, increasing subsequent stage hydrogen partial pressure (through fresh hydrogen addition), and decreasing the production of by-product light hydrocarbon gases (C_1-C_3) produced from further cracking of the 650°F liquid products.

Experimental

The feedstocks for this program are being obtained from interstage and product samples from HRI's CTSL Bench-Scale and PDU programs on Wyoming Black Thunder sub-bituminous and Illinois #6 bituminous coals.

The principal experimental systems that are being used are:

- A fixed bed microreactor with continuous liquid (slurry) and gaseous feeds.

- A 300 cc fixed bed reactor. This system represents a closer prototype to large scale equipment.

- A rapidly agitated microautoclave, 20 cc in volume, with very rapid heating and cooling. This apparatus used as a batch operation with and without catalysts is in a kinetic regime similar to a fixed bed plug flow reactor. Earlier experimental work has demonstrated kinetic effects of a pattern similar to those of prototype bench unit CTSL operations.

- A Robinson-Mahoney agitated reactor, containing a rotating catalyst basket, with a 1000 cc reaction volume. This system as a continuous flow operation corresponds to a catalytic CSTR configuration of the CTSL system with somewhat greater flexibility and simplicity of operation.

Plans

The program covers two years of activity, starting in October 1991 through September 1993. Experimental work is currently underway. Successful results from this program may be scaled to larger development units in a succeeding optional two year program.

References

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2. P. M. Yavorsky, Sakhtar and S. Friedman, "Process Developments" Fixed Bed Catalysis of Coal to Fuel Oil". American Institute of Chemical Engineers Symposium Series Vol. 70 No. 137, 1974 pp.101-105.

FIGURE 1

REACTOR CONFIGURATION AND REACTOR VOLUME

First Order Kinetics